FLUOROPHOSPHATE GLASS
AND METHOD FOR MAKING THEREOF

BACKGROUND OF THE INVENTION

This is a continuation-in-part of application Serial No. 09/892,238 filed on 06-26-2001 which application is pending.

[0001] Field of Invention: This invention relates to novel compositions of doped fluorophosphates glass. The new and improved glass compositions are particularly useful in laser glass, amplifiers and high density optical storage applications and are based on or contain $Ba(PO_3)_2$, $Al(PO_3)_3$, BaF_2 or related fluorides and MnO or R_2O_3 where R is from the group Nd, Er, Tm, Ho, Pr, Tb, Yb, Sm and Eu.

[0002] Description of Related Art: Presently most optical laser glasses are manufactured on a SiO_2 base. The SiO_2 based laser glasses have a limited refractive index of nD = 1.40 to 1.45 and a limited infrared transmission spectrum. These limitations prohibit use of SiO_2 based glasses in applications for modern laser applications such as the need for glass with efficient transparency in the near and mid infrared frequency range.

[0003] There are disclosures of fluorophosphates glass compositions in existing art; however, none of the existing glass compositions provide the efficient transmission qualities of the present invention in the near and mid infrared frequency range used in modern laser applications. Fluorophosphate laser glasses have a higher refractive index and dispersion than glasses with silicon dioxide. The fluorophosphates glasses generally have a refractive index of nD = 1.6344 to 1.6412. They can be used as the basis for creating high power lasers.

[0004] Fluorophosphate glasses are close to the phosphate glasses in terms of the degree of covalence of the dopant-ligand bond. This has been

confirmed by comparison of the Racha coefficient, B, for these glasses. The magnitude of B decreases with a decrease in size of the effective nuclear charge of free ions. The boundaries of glass formation for fluorophosphate glasses with metaphosphates of barium and aluminum and with fluorides of alkaline earth elements create a wide domain of glass forming fluorophosphates that increase in the following order Ba > Sr > Ca > Mg. The presence of barium fluoride, BaF_2, with RF_x where RF_x is from the group MgF_2, CaF_2, PbF_2 and BiF_3 effectively increases chemical durability of laser materials.

[0005] The phosphate laser glasses of varying composition due to thermal expansion and hardness properties and to low chemical durability or stability are not suited for the laser applications anticipated for the instant invention. These limitations are generally due to the presence of metaphosphates of lithium, sodium and potassium, U.S. Patent No. 3,846,142.

[0006] Existing fluorophosphates laser glass such as the system Ba PO_3F - MgF_2 - Nd_2O_3 - Ga_2O_3 - MnO have a high rate of inactive absorption of wavelength 1,064 nm, which reduces the luminescence of glass dopants. There also exist a class of fluorophosphate laser glasses that were developed on a base of metaphosphate aluminum and fluorides of metal from the first and second group of the periodic elements. The optical constant for these glasses are in the range (nD) from 1.45 to 1.59 whereas the instant invention exceeds 1.60 for greater laser efficiency, U.S. Patent No.'s 2,511,225; 2,511,227; 2,481,700 and 2,430,539.

[0007] There are several publications that discuss compositions of fluorophosphates glass; however, they do not disclose or anticipate the specific composition of the present invention. Example text references are: Journal De Physique V 4n4, April 1994, Pages 509-512, article of R. Balda, J. Fernandez and A. DePablos.; Journal of Non-Crystalline Solids, Vol. 213 - 214, June 1997, pages 245 - 250, article of J.L. Adam, N. Henry Duhamel and J.Y. Allain; and Journal of Chinese Physics Lasers, Chin. Phys. Lasers, Vol. 16., No. 4, April

1989, pages 227 - 232.

SUMMARY OF THE INVENTION

[0008] This invention is related to fluorophosphates glass compositions that are used for laser applications, amplifiers and high density optical storage. Fluorophosphate glasses offer many advantages over crystalline materials. Due to unique spectroscopic properties the fluorophosphates vitreous materials can be used for ultraviolet, visual and near infrared optics in the band of 250 to 3,500 nm.

[0009] The fluorophosphate glass contains the components Ba(PO3)2, Al(PO3)3, BaF2 and RFx where RFx is from the group MgF2, CaF2, PbF2 and BiF3 or related fluorides and MnO or R2O3 where R is from the group Nd, Er, Tm, Ho, Pr, Tb, Sm, Eu and Yb. This composition of glass has a high level of chemical durability, laser efficiency and luminescence of dopants.

[0010] These and other features, aspects and advantages of the present invention will become better understood with reference to the following drawings, description and claims.

~~BRIEF DESCRIPTION OF THE DRAWINGS~~

[0011] There are no Drawings.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0012] The following detailed description is the best currently contemplated modes for carrying out the invention. The description is not to be taken in a limiting sense, but is made merely for the purpose of illustrating the general principles of the invention.

[0013] The preferred material for the present invention are glasses based on or containing Ba(PO3)2, 10 to 60 mol %; Al(PO3)3, 10 to 60 mol %; BaF2 + RFx, 20 to 90 mol %; and MnO or R2O3, 2 to 20 weight %, where R is from the group Nd, Er, Tm, Ho, Pr, Tb, Sm, Eu and Yb. The raw compounds used for glass formation are: Metaphosphate Barium, Ba(PO3)2, and Aluminum, Al(PO3)3, which are considered chemically stable substances. When MnO or Yb2O3 are used as co-dopant sensitizers the range of dopant is 1 to 20 weight %.

[0014] Characteristics of the glass compositions indicate the duration of luminescence for neodymium ions in the laser wavelength 1064 nm is 420 to 450 msec and the half width of luminescence is 160 to 165 cm^{-1}. For erbium ions, the duration of luminescence in the laser wavelength 1535 nm is 480 to 500 msec and the half width of luminescence is 150 to 155 cm^{-1}.

[0015] A neodymium and erbium doped athermal fluorophosphate glass results from the high neodymium and erbium oxide or fluoride concentration of 5 to 20 weight %. Erbium doped fluorophosphate laser glass is more efficient than erbium doped silicate laser glass. Erbium doped fluorophosphate laser glass also has an eye safe operating wavelength of 1535 nm which makes it useful for specialized medical apparatus as well as for range finding equipment. The combination of the base materials and dopants provide an efficient laser glass in the infrared region for laser use.

[0016] The preferred glass forming compounds, Ba(PO3)2 and Al(PO3)3 are characterized as chemically stable substances. In combination they create a significant free or open volume structure due to the large ionic radii of barium (1.38°A) as in Ba(PO3)2 and BaF_2 + RFx. This allows the homogenous and regular distribution of dopant ions in a glass matrice.

[0017] The presence of BaF_2 + RFx effectively increases the chemical durability of the laser material. In the grouping of glasses according to chemical stability of non-silicate glasses relating to humidity or moisture, these glasses are considered to be stable glasses. During the melting process a chemical

integration between Ba(PO3)2 and BaF2 creates BaPO3F, monofluorophosphate barium.

[0018] The melting process is conducted in the temperature range of 1,200°C to 1,250°C in vitreous carbon crucibles in a dry argon atmosphere for 4 to 5 hours followed by an annealing temperature range of 320°C to 340°C for 8 to 10 hours. In the system of Ba(PO3)2 - Al(PO3)3 - BaF2 - RFx with dopants R, including sensitizers MnO and Yb2O3, two separate glass forming ranges were discovered as illustrated in Table I.

TABLE I

Range I (in mol %)		
Ba(PO3)2	Al(PO3)3	BaF2 + RFx
0 -100	0 -100	5 - 30
Range II (in mol %)		
Ba(PO3)2	Al(PO3)3	BaF2 + RFx
0 - 45	5 - 30	45 - 90

[0019] Examples of effective compositions and properties of the fluorophosphates laser glass for the composition Ba(PO3)2 - Al(PO3)3 - BaF2 - RFx - Nd2O3 - Er2O3 are illustrated in Table II based on mol percent and weight percent.

TABLE II

Composition of Glass (mol %)			Dopands (wt %)		Refractive	Density	Quantum Yield (%)
$Ba(PO_3)_2$	$Al(PO_3)_3$	BaF_2 +RFx	Nd_2O_3	Er_2O_3	Index(nD)	(g/cm^3)	Luminescence
40	48	10	2		1.6345	3.35	45
35	13	50	2		1.6385	3.38	60
28	10	60	2		1.6401	3.40	65
10	18	70	10		1.6412	3.45	70
40	48	10		2	1.6344	3.35	50
35	13	50		2	1.6386	3.36	63
28	10	60		2	1.6403	3.41	66
10	18	70		20	1.6410	3.43	75
5	5	90		5			

[0020] In this example ~~MnO and~~ Yb_2O_3 would be used as dopant sensitizers.

[0021] While the invention has been particularly shown and described with respect to the illustrated and preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.